Chromium-catalyzed *syn*-Stereoselective Ring-opening Arylation of 7-Oxabenzonorbornadienes

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Stereoselective synthesis of multi-functionalized 1,2-dihydronaphthalenols has attracted interest due to their usability as building blocks for synthesizing biologically active compounds.[1] Ring-opening and arylation of 7-oxabenonorbornadienes with organometallic reagents is a straightforward method to derivatize to the 1,2-dihydronaphthalenol motif[2] since the easy accessibility of 7-oxabenzonorbornadienes from furan derivatives and benzyne precursors *via* [4 + 2]-cycloaddition reaction.[3] Among the organometallic reagents used in this reaction, Grignard reagents are the most readily available carbon nucleophiles from the corresponding aryl halides and magnesium powders; however, they were less applicable due to the lower tolerance to the functional groups due to the high reactivity of the Grignard reagents.[2c] Herein, we report that chromium complexes served as catalysts for *syn*-stereoselective ring-opening arylation of 7-oxabenzonorbornadienes with aryl Grignard reagents, giving *syn*-2-aryl-1,2-dihydronaphthalen-1-ols. Chromium complexes exhibited extremely high catalytic activity, reaching to the turn-over number up to 25,000 as the highest turn-over number among the chromium-catalyzed C-C bond formation reactions. In this reaction, we demonstrated a versatility of a rather simple protocol of successive *in situ*-aryl Grignard formation followed by chromium-catalyzed reactions; aryl Grignard reagents bearing various reactive functional groups were applicable to the chromium-catalyzed ring-opening arylation at -20 °C, giving *syn*-2-aryl-1,2-dihydronaphthalen-1-ols with the corresponding functionality.[4] Substrate scope and the reaction mechanism are disclosed in this presentation.

【References】

(1) a) Snyder, S. E.; Aviles-Garay, F. A.; Chakraborti, R.; Nichols, D. E.; Watts, V. J.; Mailman, R. B. *J. Med. Chem.* **1995**, *38*, 2395－2409. b) Lautens, M.; Rovis, T. *J. Org. Chem.* **1997**, *62*, 5246－5247. (2) a) Kumar, S. V.; Yen, A.; Lautens, M.; Guiry, P. J. *Chem. Soc. Rev.*, **2021**, *50*, 3013－3093. b) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48. c) Nakamura, M.; Matsuo, K.; Inoue, T.; Nakamura, E. *Org. Lett.* **2003**, *5*, 1373－1375. (3) Sanz, R. *Org. Prep. Proced. Int.*, **2008**, *40*, 215－291. (4) Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3333－3336.